PATENT ABSTRACTS OF JAPAN

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(71)Applicant : FUJI XEROX CO LTD
(72)Inventor : IMAI AKIRA
SATO KATSUHIRO
HIROSE HIDEKAZU

(54) LIGHT SEMICONDUCTOR ELECTRODEPHOTOELECTRIC CONVERSION DEVICE AND PHOTOELECTRIC CONVERSION METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To improve photoelectric conversion efficiencystability and durability by providing an adsorbing film by at least one kind of perylene derivative on a base material of a semiconductor.
SOLUTION: A light semiconductor electrode has an adsorbing film by at least one kind of perylene derivative expressed by either of formula I and formula II on a base material of a semiconductor. In the formula I and the formula IIA represents a bivalent group expressed by formula III. In the formula IIIX represents a hydrogen atoma halogen atom or an alkyl group having the carbon number of 1 to 4Y represents a group bondable by reacting with the semiconductorand is desirably a group expressed by -(CH2)n-Z. HereZ is -COOH or -NH2and (n) is an integer of 0 to 4. Titanium oxide is particularly desirable as the semiconductor from the viewpoint of a photoelectric conversion characteristicchemical stability and manufacturing facility. The light semiconductor electrode can be manufactured by soaking the base material of this semiconductor in a solution of the perylene derivative expressed by the formula I or the formula II.

CLAIMS

[Claim(s)]
[Claim 1]An optical semiconductor electrode which has an adsorption film by at least one sort of a perylene derivative expressed with either a following general formula (Ia) and a general formula (Ib) on a substrate of a semiconductorand is characterized by things.
A general formula (Ia)
[Formula 1]

General formula (Ib)
[Formula 2]

HoweverA expresses the divalent basis expressed with following general formula (II) among said general formula (Ia) and a general formula (Ib).
General formula (II)
[Formula 3]

HoweverX express the alkyl group of a hydrogen atoma halogen atomor the carbon numbers 1-4 among said general formula (II). Y expresses the basis which reacts to said semiconductor and can be combined.
[Claim 2]the optical semiconductor electrode according to claim 1 whose Y is $-(CH_2)_n-Z$ and a basis come out of and expressed in a perylene derivative expressed with either a general formula (Ia) and a general formula (Ib). Howeverin said basisZ expresses -COOH or $-NH_2$. n expresses an integer of 0-4.
[Claim 3]The optical semiconductor electrode according to claim 1 or 2 whose semiconductor is titanium oxide.
[Claim 4]A photoelectric conversion device which has at least a connecting means which connects an electrode of a couple immersed into an electrolytic solutionand an electrode of this couple so that energization is possibleand is characterized by one side of an electrode of this couple being the optical semiconductor electrode according to any one of claims 1 to 3.
[Claim 5]In a photoelectric conversion method of making an electrode of a couple mutually connected so that energization was possible immersed into an electrolytic solutionand producing a photoelectric conversion reaction by irradiating at least one side of an electrode of this coupleA photoelectric conversion methodwherein an electrode which

irradiates with said light is the optical semiconductor electrode according to any one of claims 1 to 3.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the optical semiconductor electrode which is efficiently availableand is excellent in photoelectric conversion efficiencystabilityenduranceetc. and can carry out sunlight by low costthe photoelectric conversion device using itand the photoelectric conversion method.
[0002]
[Description of the Prior Art]In recent yearsuse of sunlight attracts attention as an energy resource replaced with fossil fuelssuch as petroleum and coal. As a photoelectric conversion device which transforms light energy into electrical energy directlythe dry type solar cell in which p-n junction was formed on inorganic semiconductorssuch as silicon and gallium arsenideis known widelyand it is already put in practical use as a power supply of the object for remote placesor a portable electronic deviceetc. Howeversince the energy and cost which the manufacture takes are very high in the case of said dry type solar cellthere is a problem that it is difficult to use widely.
[0003]The wet solar cell whichon the other handused the photoelectrochemical reaction which occurs by the interface of a semiconductor and an electrolytic solution as another photoelectric conversion device which transforms light energy into electrical energy is known. Semiconductors used in said wet solar cellsuch as titanium oxide and tin oxideAs compared with the silicon used in said dry type solar cellgallium arsenideetc. it can manufacture at far low energy and costand titanium oxide is especially expected as a future energy conversion material from excelling in both sides of a photoelectric transfer characteristic and stability. Howeverit cannot be said that they can use only the ultraviolet radiation which is about 4% of sunlightbut their conversion efficiency is high enough since stable optical semiconductorssuch as titanium oxidehave the band gap as large as not less than 3 eV.
[0004]On the surface of this optical semiconductoras sensitizing dye Thenorganic coloring mattersuch as cyanine dye and a xanthene dyeTo make organometallic complexessuch as a tris(22'-bipyridyl) ruthenium (II)

complexadsorband to carry out spectral sensitization is triedit is known that it is a method effective in improvement in conversion efficiency (T. -- OsaM. FujihiraNature. and 264349 (1976).) Brian O'ReganMichael GratzelNature353736 (1991)JP1-220380Aetc.

[0005]Howeverneither cyanine dye nor a xanthene dye is enough in respect of stabilityenduranceetc. and on the other handalthough the organic ruthenium complex is excellent in respect of conversion efficiencystabilityetc. it has the problem of being expensive. Thereforethe actual condition is that high conversion efficiencythe optical semiconductor electrode cheap at high durabilitythe photoelectric conversion deviceand the photoelectric conversion method are not yet provided.

[0006]

[Problem(s) to be Solved by the Invention]This invention solves many problems in said formerand makes it a technical problem to attain the following purposes. That isan object of this invention is to provide the optical semiconductor electrodephotoelectric conversion deviceand the photoelectric conversion method of it being efficiently availableand excelling in photoelectric conversion efficiencystabilityenduranceetc. and carrying out sunlight by low cost.

[0007]

[Means for Solving the Problem]Said The means for solving a technical problem is as follows. That isit is an optical semiconductor electrode which has an adsorption film by at least one sort of a perylene derivative expressed with either a following general formula (Ia) and a general formula (Ib) on a substrate of <1> semiconductorand is characterized by things.

[0008]General formula (Ia)

[Formula 4]

[0009]General formula (Ib)

[Formula 5]

[0010]HoweverA expresses the divalent basis expressed with following general formula (II) among said general formula (Ia) and a general formula (Ib).

[0011]General formula (II)

[Formula 6]

[0012]HoweverX express the alkyl group of a hydrogen atoma halogen atomor the carbon numbers 1-4 among said general formula (II). Y expresses the basis which reacts to said semiconductor and can be combined.
an optical semiconductor electrode given in a claim <1> whose Y is -$(CH_2)_n$-Z and a basis come out of and expressed in a perylene derivative expressed with either <2> general formulas (Ia) and a general formula (Ib). Howeverin said basisZ expresses -COOH or $-NH_2$. n expresses an integer of 0-4.
<3> semiconductors are optical semiconductor electrodes given in the above <1> or <2> which is titanium oxide.
[0013]It has at least a connecting means which connects an electrode of a couple immersed into <4> electrolytic solutionsand an electrode of this couple so that energization is possibleand one side of an electrode of this couple is a photoelectric conversion device characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <3>.
[0014]<5> In a photoelectric conversion method of making an electrode of a couple mutually connected so that energization was possible immersed into an electrolytic solutionand producing a photoelectric conversion reaction by irradiating at least one side of an electrode of this coupleAn electrode which irradiates with said light is the photoelectric conversion method characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <3>.
[0015]
[Embodiment of the Invention](Optical semiconductor electrode) The optical semiconductor electrode of this invention has an adsorption film by at least one sort of a perylene derivative expressed with either a following general formula (Ia) and a general formula (Ib) on the substrate of a semiconductor.
[0016]- Substrate of a semiconductor - As said semiconductortitanium oxidetin oxidetungstic oxidea zinc oxideindium oxideniobium oxidestrontium titanateetc. are mentionedfor example. These may be used by an one-sort independent and may use two or more sorts together. Especially in this inventionthe reasons of a photoelectric transfer characteristicchemical stabilitymanufacture easeetc. to titanium oxide is preferred also in these.
[0017]There is no restriction in particular about the shape of the substrate of said semiconductorstructureand a sizeand it can choose suitably according to the purpose. In this inventionit may be a

substrate which consists only of said semiconductorand may be a substrate which forms the coating membrane of said semiconductor on an electrode with publicly known tabular [by the transparent electrode by ITO glassNesa glassetc. platinumcopperblack leadetc.] or mesh state electrode etc. for example. In the case of the latter substratethis coating membrane may be provided the whole surface on said publicly known electrodeand may be provided in part.

[0018]- Adsorption film - Said adsorption film is formed of at least one sort of a perylene derivative expressed with either a following general formula (Ia) and a general formula (Ib).

[0019]General formula (Ia)

[Formula 7]

[0020]General formula (Ib)

[Formula 8]

[0021]HoweverA expresses the divalent basis expressed with following general formula (II) among said general formula (Ia) and a general formula (Ib).

[0022]General formula (II)

[Formula 9]

[0023]HoweverX express the alkyl group of a hydrogen atoma halogen atomor the carbon numbers 1-4 among said general formula (II). The basis which expresses the basis which Y reacts to said semiconductor and can be combinedand is expressed with $-(CH_2)_n-Z$ (hereZ expresses -COOH or $-NH_2$.) n expresses the integer of 0-4. It is desirable and especially the basis expressed with $-(CH_2)_n-COOH$ (n expresses the integer of 0-4.) is preferred.

[0024]A desirable example of a perylene derivative expressed with either said general formula (Ia) and a general formula (Ib) is shown below.

[0025]General formula (Ia)

[Formula 10]

[0026]General formula (Ib)

[Formula 11]

[0027]
[Table 1]

[0028]In the perylene derivative expressed with said general formula (Ia) and a general formula (Ib)Z is $-(CH_2)_n-COOH$ (n). The integer of 0-4 is expressed. The perylene derivative which is a basis expressed is compoundable by making a 34910-perylene tetracarboxylic anhydride and the compound expressed with following general formula (III) react.
[0029]General formula (III) [Formula 12]

[0030]Howeversaid general formula (III) X express the alkyl group of a hydrogen atoma halogen atomor the carbon numbers 1-4 inside. n expresses the integer of 0-4.
[0031]The perylene derivative which is a basis as which Z is expressed in $-NH_2$ in the perylene derivative expressed with said general formula (Ia) and a general formula (Ib)After making a 34910-perylene tetracarboxylic anhydride and the compound expressed with following general formula (IV) reactIt is compoundable using reducing agentssuch as zinc and stannous chlorideby changing the nitro group ($-NO_2$) of this general formula (IV) Naka into an amino group ($-NH_2$).
[0032]General formula (IV) [Formula 13]

[0033]HoweverX express the alkyl group of a hydrogen atoma halogen atomor the carbon numbers 1-4 among said general formula (IV).
[0034]In a perylene derivative expressed with said general formula (Ia) and a general formula (Ib)Z is $-(CH_2)_n-NH_2$ (n). An integer expressed with 0-4 is expressed. A perylene derivative which is a basis expressedAfter making a 34910-perylene tetracarboxylic anhydride and a compound expressed with following general formula (V) reactIt is compoundable by changing a cyano group (-CN) of this general formula (V) Naka into a basis expressed with $-CH_2NH_2$ using reducing agentssuch as lithium aluminum hydride.
[0035]General formula (V)
[Formula 14]

[0036]HoweverX express the alkyl group of a hydrogen atoma halogen

atomor the carbon numbers 1-4 among said general formula (V). n expresses the integer expressed with 0-4.

[0037]Can manufacture cheaply the perylene derivative expressed with said general formula (Ia) or (Ib)and it is excellent in chemical stability and enduranceand is excellent in the holdout in the base material surface of said semiconductorand can carry out spectral sensitization of the optical semiconductor electrode stably and efficient over a long period of time.

[0038](Production of an optical semiconductor electrode) An optical semiconductor electrode of this invention is producible by making a substrate of said semiconductor immersed into a solution which dissolved at least one sort of a perylene derivative expressed with either said general formula (Ia) and a general formula (Ib)for example. When preparing said solutionin order to increase the solubility of said perylene derivativeit is preferred to add an alkali or acid in proper quantity into said solution.

[0039]In the case of a perylene derivative which is a basis as which Z is expressed in $-(CH_2)_n-COOH$ (n expresses an integer of 0-4.)as a substance added into said solutionan alkali is preferred in a perylene derivative expressed with said general formula (Ia) and a general formula (Ib). As said alkaliwhat can form a salt of said perylene derivativessuch as organic aminesuch as quaternary ammonium hydroxidesuch as inorganic alkalisuch as a potassium hydrateand tetraethylammoniumhydroxideand tetraethyl amineand fusibility is mentioned suitablyfor example. In this inventionsaid perylene derivative may be beforehand prepared as a salt with these alkalis.

[0040]In the case of a perylene derivative which is a basis as which Z is expressed in $-(CH_2)_n-NH_2$ (n expresses an integer of 0-4.)as a substance added into said solutionacid is preferred in a perylene derivative expressed with said general formula (Ia) and a general formula (Ib). As said acidwhat can form a salt of said perylene derivativessuch as organic acidsuch as inorganic acidsuch as chloride and sulfuric acidacetic acidtrifluoroacetic acidand p-toluenesulfonic acidand fusibility is mentioned suitablyfor example. In this inventionsaid perylene derivative may be beforehand prepared as a salt with these acid.

[0041]If a substrate of said semiconductor is taken out after said immersion and it dries after washing with arbitrary solventsan optical semiconductor electrode which an adsorption film by at least one sort of said perylene derivative reacts to a base material surface of said semiconductorand it comes to fix to it will be obtained.

[0042]As a solvent which dissolves at least one sort of a perylene derivative expressed with either said general formula (Ia) and a general formula (Ib)For examplevarious organic solventssuch as amide system solventssuch as ketone solventsuch as alcoholic solventsuch as methanol and isopropyl alcoholacetoneand methyl ethyl ketoneand N.N-dimethylformamideor these mixed solventsare mentioned. These may be used by an one-sort independent and may use two or more sorts together. Also in thesealcoholic solvent is preferred.
[0043]Although at least one sort of adsorption reactions of said perylene derivative to a base material surface of said semiconductor may be performed at a room temperaturethey may be heated to temperature below the boiling point of a solvent if needed.
[0044]An optical semiconductor electrode of this invention produced by making it above can be used conveniently for the following photoelectric conversion devices and photoelectric conversion methods of this invention.
[0045](Photoelectric conversion device) A photoelectric conversion device of this invention has at least a connecting means which connects an electrode of a couple immersed into an electrolytic solutionand an electrode of this couple so that energization is possible. Said photoelectric conversion device may be provided with apparatus suitably selected according to the purpose etc. outside an electrode of said coupleand said connecting means.
[0046]-A pair of electrodes - One side in an electrode of said couple is an optical semiconductor electrode of said this inventionand another side is a counterelectrode. As said counterelectrodeif electrochemically stablethere will be no restriction in particularand according to the purposeit can choose from a publicly known thing suitablyfor examplecan choose from transparent electrodessuch as flat electrodessuch as platinumgoldand black leador ITO glassand Nesa glassetc. suitably according to the purpose.
[0047]- Connecting means - As long as it has a function in which an electrode of said couple can be connected as said connecting means so that energization is possiblethere is no restriction in particular and can choose suitably according to the purposebut. For examplea wire rod which consists of conductive materialssuch as a publicly known leadvarious metalcarbonand a metallic oxidein itselfa platea printed filmor a vacuum evaporation film is mentioned. This connecting means is connected to an electrode of said couple so that energization is possible. A photoelectric conversion device of the above this invention can be used conveniently for a photoelectric conversion method of the

following this inventions.
[0048](A photoelectric conversion method) A photoelectric conversion method of this invention makes an electrolytic solution immerse an electrode of a couple mutually connected so that energization was possibleand produces a photoelectric conversion reaction by irradiating at least one side of an electrode of this couple. Those in an electrode of said couple who irradiate with light are the optical semiconductor electrodes of said this inventionand another side is said counterelectrode. Said connecting means can be used for connecting an electrode of this couple so that energization is possible. For this reasonas an electrode of said couple mutually connected so that energization was possiblea photoelectric conversion device of said this invention can be used.
[0049]- Electrolytic solution - Although there is no restriction in particular and it can choose suitably as said electrolytic solutionFor examplesaltssuch as potassium chloridea lithium chloridepotassium carbonateand tetraethylammonium perchlorateNonaqueous solvent solutionssuch as solutionsuch as acidssuch as alkalisuch as sodium hydroxide and potassium carbonatesulfuric acidand chlorideor these mixturesor alcoholand propylene carbonateetc. are mentioned. These may be used by an one-sort independent and may use two or more sorts together. In this inventiona compound in which it is the purpose of attaining stabilization of the photoelectric current characteristicand also potassium iodidep-benzoquinoneetc. produce an oxidation-reduction reaction reversibly may be added to said electrolytic solution.
[0050](Photoelectric conversion reaction) In a photoelectric conversion device and a photoelectric conversion method of this inventiona photoelectric conversion reaction can be produced as follows. That isan above-mentioned electrodei.e. said optical semiconductor electrodeand said counterelectrode of a couple are first immersed into said nature solution of an electric field. Nextthis optical semiconductor electrode is irradiated with monochromatic light of a 300-650-nm wavelength bandwhite light which includes one in this wavelength band of zonesor multicolor light. Thenlight energy is transformed into electrical energy in this optical semiconductor electrode. At this timeit is changed into electrical energy very efficiently to light energy of visible light of not only ultraviolet radiation of a wavelength band below 300-400 nm but a 400-650-nm wavelength band.
[0051]Even visible light which cannot be used with metallic-oxide independentsuch as titanium oxideby using said optical semiconductor electrode in this invention can use effectivelyAs a resultsynthetic use

of lightssuch as sunlightis attained and light energiessuch as sunlightcan be transformed into electrical energy at high efficiency. And in said optical semiconductor electrode to be usedAn adsorption film by at least one sort of said chemical very stable perylene derivative has adhered to a base material surface of said semiconductor firmlyand this adsorption filmSince it is not easily desorbed from this optical semiconductor electrodethe characteristic of this optical semiconductor electrode is stabilized for a long period of timecan be maintainedand can always perform a photoelectric conversion reaction efficiently.

[0052]

[Example]Hereafteralthough the example of this invention is describedthis invention is not limited to these examples at all.

[0053](Example 1)

- 25 ml of production-alt. titanic acid tetraisopropyl of the optical semiconductor electrode was gradually added into the mixed solution of 150 ml of deionized waterand the concentrated nitric acid 1.54g (specific gravity: 1.38)agitating violently. Temperature up was carried out to 80 **continuing churning furthermorechurning was continued at the temperature for 8 hoursand the milky stable titanium oxide colloidal solution was obtained. The above operation was performed under the dry nitrogen air current. This colloidal solution was condensed until 40 ml of viscous fluids remained at 30 ** under decompression of 30mmHg. In this waythe obtained viscous fluid was used as the titanium oxide colloidal solution.

[0054]Said titanium oxide colloidal solution was coated with the spin coat method on ITO/glass base material as an electrodeand was calcinated at 500 ** for 1 hour. This operation was repeated 3 times and the titanium oxide enveloping layer about 1.0 micrometer thick was formed on this ITO/glass base material. When the crystal structure of the obtained titanium oxide enveloping layer was checked with the X-ray diffraction methodit was checked that it is a mixture of an anatase and a rutile type.

[0055]After 100 mg of mixtures and the potassium hydrate 0.5g of a perylene derivative which are expressed with said general formula (Ia-1) and a general formula (Ib-1) in ITO/glass base material in which said titanium oxide enveloping layer was formed are immersed in the solution which dissolved in 50 ml of ethanol at 70-80 ** for 1 hourmethanolwaterand acetone -- subsequentlywith methanolit washed one by one and natural seasoning was carried out. Thenthe lead was connected to ITO/glass base material in which the titanium oxide enveloping layer is not formedboth terminal area was adhered with the epoxy resinand the

optical semiconductor electrode as shown in drawing 1 was produced.
[0056]When the ultraviolet and visible absorption spectrum of the produced optical semiconductor electrode is investigatedas shown in drawing 2The same spectrum data as the ultraviolet and visible absorption spectrum by the mixture of the perylene derivative expressed with said general formula (Ia-1) and a general formula (Ib-1) is obtainedIt was checked that the adsorption film by the mixture of the perylene derivative expressed with said general formula (Ia-1) and a general formula (Ib-1) on said titanium oxide enveloping layer is being fixed.
[0057]the optical semiconductor electrode 1 shown in drawing 1 -- the glass base material 2 top -- the ITO layer 3 and the titanium oxide enveloping layer 4 -- andLaminating the adsorption film 5 by the mixture of the perylene derivative expressed with said general formula (Ia-1) and a general formula (Ib-1) in this orderthe end of these lamination sides and the terminal area with the lead 7 were covered with the epoxy resin as the adhesive agent 6and have adhered with it.
[0058]- The optical semiconductor electrode 1 produced as mentioned above as shown in production-drawing 3 of a photoelectric conversion deviceThe platinum electrode selected as the counterelectrode 9 and the saturation Carmelo electrode selected as the reference electrode 10 were immersed in the electrolytic solution 11 in the transparent glass cell 13each electrode was connected to the potentiostat 12using the lead 8 as a connecting meansand the photoelectric conversion device was produced. As said electrolytic solution 110.1M sodium sulfate / 0.02M potassium iodide solution was used. The lead 8 is connected to each electrode and energization has become possible. The lead 8 is accommodated in the glass tube. As the reference electrode 10this photoelectric conversion device is equipped with the saturated calomel electrode so that energization is possible. The photoelectric conversion device was produced by the above.
[0059]- holding in the photoelectric conversion device obtained by more than photoelectric conversion reaction -so that the potential of said optical semiconductor electrode may be set to 0V to said reference electrode -- white light (the xenon lamp of 500W.) It irradiated with illumination 4000lux or 550-nm monochromatic light (1 mW/cm^2) from the back side of said optical semiconductor electrode. The value of the photoelectric current by the photoelectric conversion reaction produced at this time was measured with the potentiostat. The measurement result was shown in Table 2.
[0060](Example 2) In Example 1the mixture of the perylene derivative

expressed with said general formula (Ia-1) and a general formula (Ib-1)Like Example 1the outside replaced with the mixture of the perylene derivative expressed with said general formula (Ia-3) and a general formula (Ib-3) produced the optical semiconductor electrode and the photoelectric conversion devicerespectivelyproduced the photoelectric conversion reactionand measured photoelectric current. The measurement result was shown in Table 2.

[0061](Comparative example 1) The outside which did not make the mixture of the perylene derivative expressed with said general formula (Ia-1) and a general formula (Ib-1) adsorb on said titanium oxide enveloping layer in Example 1Like Example 1the optical semiconductor electrode and the photoelectric conversion device were producedrespectivelythe photoelectric conversion reaction was producedand photoelectric current was measured. The measurement result was shown in Table 2.

[0062](Comparative example 2) It replaces with the mixture of the perylene derivative expressed with said general formula (Ia-1) and a general formula (Ib-1) in Example 1Like Example 1the outside which used 2457-tetraiodofluorescein (erythrosin B) produced the optical semiconductor electrode and the photoelectric conversion devicerespectivelyproduced the photoelectric conversion reactionand measured photoelectric current. The measurement result was shown in Table 2.

[0063]

[Table 2]

[0064]

[Effect of the Invention]According to this inventionmany problems in said former are solvable. According to this inventionthe optical semiconductor electrodephotoelectric conversion deviceand the photoelectric conversion method of it being efficiently availableand excelling in photoelectric conversion efficiencystabilityenduranceetc. and carrying out sunlight by low cost can be provided.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]Drawing 1 is a section approximate account figure of the optical semiconductor electrode in Example 1.

[Drawing 2]Drawing 2 is data of the ultraviolet and visible absorption spectrum of the optical semiconductor electrode in Example 1.
[Drawing 3]Drawing 3 is an approximate account figure of the photoelectric conversion device in Example 1.
[Description of Notations]
1 Optical semiconductor electrode
2 Glass base material
3 ITO layer
4 Titanium oxide enveloping layer
5 Adsorption film
6 Adhesive agent
7 Lead
9 Counterelectrode
10 Reference electrode
11 Electrolytic solution
12 Potentiostat
13 Glass cell